

The crystal structure refinements of the strontium and barium orthophosphates

Kazumasa SUGIYAMA* and Masayasu TOKONAMI

*Mineralogical Institute, Faculty of Science, University of Tokyo,
Hongo, Tokyo 113, Japan*

Abstract

The crystal structure refinements of $\text{Sr}_3(\text{PO}_4)_2$ [$a = 5.3901(8)$, $c = 19.785(5)\text{\AA}$; space group $R\bar{3}m$] and $\text{Ba}_3(\text{PO}_4)_2$ [$a = 5.6038(7)$, $c = 21.000(5)\text{\AA}$; space group $R\bar{3}m$] have been carried out by means of the single-crystal diffraction data and the final $R(R_w)$ factors have been converged to 0.0299 (0.0309) and 0.0296 (0.0335), respectively. The rod sequence of coordination polyhedra, $\text{PO}_4\text{-M}(2)\text{O}_{10}\text{-M}(1)\text{O}_{12}\text{-M}(2)\text{O}_{10}\text{-PO}_4$, where $\text{M} = \text{Sr}$ or Ba , is characteristic in these structures. The $\text{M}(1)\text{O}_{12}$ and $\text{M}(2)\text{O}_{10}$ polyhedra show smaller distortion with increase in the ionic radius of the constituent elements.

Introduction

The orthophosphates of strontium and barium have been reported to be isomorphous with orthovanadates and orthoarsenates of the same alkaline-earth elements (Zachariasen, 1948; Durif, 1959; Süssé and Burger, 1970). Recently the high pressure analogue of $\text{Ca}_3(\text{PO}_4)_2$ has been revealed to be isostructural with these materials (Roux *et al.*, 1978), and this phase has been suggested as an important host for very large lithophile elements in the lower part of the upper mantle of the earth (Murayama *et al.*, 1986; Sugiyama and Tokonami, 1988). The crystal-chemical features of this structural type of materials are of great interest not only from the crystallographic but also from the geochemical point of view. The crystal structures of strontium and barium orthophosphates, however, were determined on the basis of the quantitative estimation of powder X-ray diffraction data (Zachariasen, 1948) and the accuracy of the structural parameters does not allow to discuss the detailed crystal chemistry of this type of materials. Therefore, we have undertaken the structure refinements of these materials based on single-crystal diffraction intensities collected on a four-circle diffractometer. The results are described below.

**)present address: Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Aoba-ku, Sendai 980 Japan.*

Reprint requests to Dr. K. Sugiyama.

Experimental

Mixtures of reagent-grade BaCO_3 , SrCO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ corresponding to the chemical compositions of $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Ba}_3(\text{PO}_4)_2$ were prepared. They were calcined at about 1000°C . After grinding the calcined products into powder, they were pressed into pellets and heated again at 1400°C for 40 hours. Then, samples were slowly cooled to 1250°C and kept at that temperature for over 4 days. With this method, single crystals of both $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Ba}_3(\text{PO}_4)_2$ larger than $50\text{ }\mu\text{m}$ in size were successfully synthesized.

Intensity data collection was performed with $\text{MoK}\alpha$ radiation on an automated four-circle diffractometer (RIGAKU AFC5), using a pyrolytic graphite monochromator in the incident beam path. The lattice parameters were determined by the least-squares method, using twenty-five 2θ values between 20° and 30° measured with $\text{MoK}\alpha$ radiation (0.71073 \AA). The obtained values agree well with those reported in JCPDS cards No. 24-1008 and No. 25-28 for $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Ba}_3(\text{PO}_4)_2$, respectively. The ω - 2θ scan technique was used to measure three of twelve possible equivalent sets of diffraction intensities up to $2\theta = 90^\circ$. These sets of intensity data were corrected for Lorentz and polarization effects and subjected to absorption correction using the program of ACACA (Wuensch and Prewitt, 1965). Averaging the structure factors of equivalent reflections greater than $3\sigma |F_{\text{obs}}|$, where $\sigma |F_{\text{obs}}|$ is the standard deviation estimated by counting statistics, resulted in the independent data sets for the following structure refinements. The refinements were carried out using the least-squares program LINUS (Coppens

TABLE 1. Crystallographic and experimental data.

Chemical composition	$\text{Sr}_3(\text{PO}_4)_2$	$\text{Ba}_3(\text{PO}_4)_2$
Crystal size (mm)	$0.08 \times 0.10 \times 0.10$	$0.06 \times 0.08 \times 0.08$
Space group	$R\bar{3}m$	$R\bar{3}m$
$a(\text{\AA})$	$5.3901(8)$	$5.6038(7)$
c	$19.785(5)$	$21.000(5)$
Volume(\AA^3)	$497.8(1)$	$571.1(1)$
D_c (g/cm^3)	4.533	5.252
Radiation	$\text{Mo K}\alpha$	$\text{Mo K}\alpha$
μ for $\text{Mo K}\alpha$ (cm^{-1})	238.0	157.9
$G_{\text{iso.}}$ ($\times 10^{-5}$)	$0.38(10)$	$0.32(7)$
Maximum 2θ ($^\circ$)	90	90
Number of measured reflections	1029	1304
Number of used reflections	322	376
R (%)	2.99	2.96
wR (%)	3.09	3.35

and Hamilton, 1970) assuming the space group to be $R\bar{3}m$ reported by Zachariasen (1948). The anisotropic refinements with corrections for isotropic extinction converged at the values of R and R_w as given in Table 1. Neutral atomic form factors and values for dispersion terms were provided by *International Tables for X-ray Crystallography* (1974). The experimental conditions and crystallographic data are summarized in Table 1.

Results and discussion

The final atomic parameters and the selected interatomic distances are listed in Table 2 and 3, respectively. Since the structural aspects of the present interest were fully reported by Süss and Burger (1970), only the essential features are described below for the convenience of the following discussion. The structure is characterized by its

TABLE 2. Atomic coordinates ($\times 10^4$), anisotropic temperature factors ($\times 10^4$) and equivalent temperature factors of $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Ba}_3(\text{PO}_4)_2$.

		$\text{Sr}_3(\text{PO}_4)_2$	$\text{Ba}_3(\text{PO}_4)_2$
P	6(c)		
	z	4065(1)	4075(1)
	β_{11}	38(5)	72(7)
	β_{33}	2.8(3)	2.7(3)
	$B_{\text{eq.}}$	0.37	0.61
M(1)	3(a)		
	β_{11}	105(4)	106(3)
	β_{33}	2.5(2)	2.9(1)
	$B_{\text{eq.}}$	0.74	0.83
M(2)	6(c)		
	z	2065.3(3)	2086.0(2)
	β_{11}	65(3)	69(2)
	β_{33}	2.8(1)	3.8(1)
	$B_{\text{eq.}}$	0.52	0.66
O(1)	6(c)		
	z	3296(2)	3341(3)
	β_{11}	163(22)	125(25)
	β_{33}	2.9(9)	5.3(11)
	$B_{\text{eq.}}$	1.10	1.09
O(2)	18(h)		
	x	-1563(3)	-1502(4)
	z	4329(1)	4324(2)
	β_{11}	79(15)	91(19)
	β_{33}	5.0(6)	5.9(5)
	β_{12}	56(9)	62(11)
	β_{13}	1(1)	1(2)
	$B_{\text{eq.}}$	0.65	0.85

*) The anisotropic temperature factors are in the form:
 $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$.

TABLE 3. Interatomic distances (Å) and angles (°) of $\text{Sr}_3(\text{PO}_4)_2$ and $\text{Ba}_3(\text{PO}_4)_2$

	$\text{Sr}_3(\text{PO}_4)_2$	$\text{Ba}_3(\text{PO}_4)_2$
P-O(1)	1.522(6)	1.542(8)
-O(2) (x3)	1.549(2)	1.549(2)
O(1)-P-O(1) (x3)	2.511(5)	2.528(7)
	109.7(1)	109.7(2)
O(2)-P-O(2) (x3)	2.527(2)	2.525(3)
	109.3(1)	109.2(2)
M(1)-O(1)i (x6)	3.1128(5)	3.2354(3)
-O(2)i (x6)	2.571(2)	2.737(2)
O(1)i -M(1)-O(1)vii (x6)	3.116(1)	3.2354(3)
	60.06(2)	60.00(1)
O(1)i -M(1)-O(2)i (x6)	2.511(5)	2.528(6)
	51.4(1)	49.2(1)
O(1)i -M(1)-O(2)iii (x12)	3.296(4)	3.504(5)
	70.2(1)	71.3(1)
O(2)i -M(1)-O(2)ii (x6)	2.863(2)	3.079(3)
	67.7(1)	68.5(1)
M(2)-O(1)	2.435(6)	2.636(8)
-O(2)iv (x6)	2.750(1)	2.858(1)
-O(2)i (x3)	2.686(2)	2.906(2)
O(1) -M(2)-O(2)iv (x6)	3.296(4)	3.504(5)
	78.68(4)	79.2(1)
O(2)iv-M(2)-O(2)v (x3)	2.863(2)	3.079(3)
	62.7(1)	65.2(1)
O(2)iv-M(2)-O(2)vi (x3)	2.527(2)	2.525(3)
	54.7(1)	52.4(1)
O(2)iv-M(2)-O(2)ii (x6)	3.031(3)	3.190(5)
	67.8(1)	67.2(1)
O(2)i -M(2)-O(2)ii (x3)	2.863(2)	3.079(3)
	64.4(1)	64.0(1)

Symmetry Code none) x, y, z i) $x+1/3, y-1/3, z-1/3$ ii) $-y+1/3, x-y+2/3, z-1/3$
iii) $y-1/3, -x+y-2/3, -z+1/3$ iv) $-x+1/3, -y+2/3, -z+2/3$
v) $y+1/3, -x+y-1/3, -z+2/3$ vi) $x-y+1/3, x+2/3, -z+2/3$
vii) $-x+2/3, -y+1/3, -z+1/3$

translationally interconnected rod sequences of coordination polyhedra, $\text{PO}_4\text{-M(2)O}_{10}\text{-M(1)O}_{12}\text{-M(2)O}_{10}\text{-PO}_4$ (M = Sr or Ba in this case), which are schematically shown in Fig. 1. The M(1) atom is surrounded by twelve oxygens and shares two triangular faces with neighbouring M(2) coordination polyhedra. The M(2) atom is in a ten-fold coordination and shares a vertex O(1), with a phosphorus tetrahedron. This M(2)-O(1) distance, which is shortest among the ten, will be inspected further with the aid of the *O'Keeffe-Voronoi polyhedron*.

The application of the *O'Keeffe-Voronoi polyhedron* (Takéuchi and Haga, 1984) is very convenient to clarify the geometrical features of the coordination polyhedra. Let

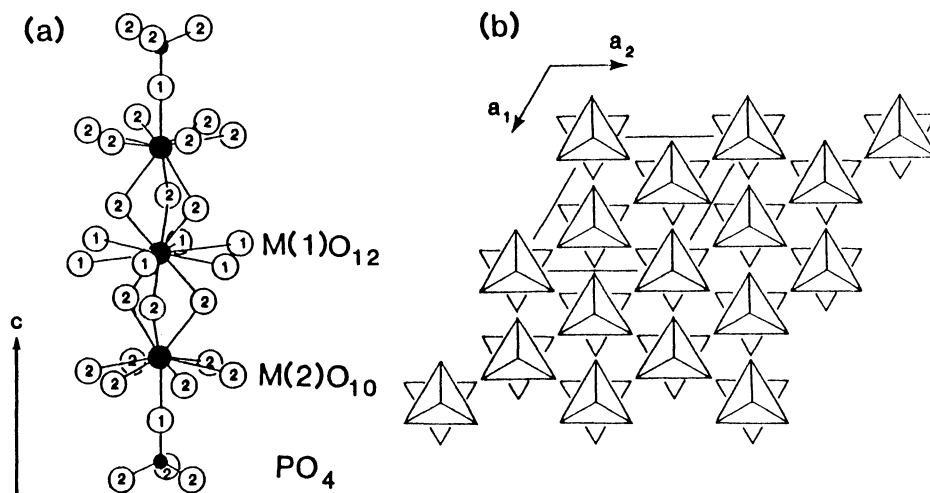


FIG. 1. a) The schematic description of the typical rod sequence of coordination polyhedra: PO₄-M(2)O₁₀-M(1)O₁₂-M(2)O₁₀-PO₄. b) A schematic c-axis projection of the Ba₃(PO₄)₂ and Sr₃(PO₄)₂, showing the distribution of the PO₄ tetrahedra.

θ_i be the solid angle subtended by the i -th face at the central cation. Then, the θ_i may be used to evaluate the relative contribution of i -th oxygen to the central cation. Using such θ_i as the weight for each bond, the weighted mean bond lengths (Takéuchi, 1984) were calculated and compared with the usual unweighted mean bond lengths. Information about the *O'Keeffe-Voronoi polyhedron* of M(1) and M(2) sites are summarized in Table

TABLE 4. Coordination polyhedra of Sr₃(PO₄)₂ and Ba₃(PO₄)₂ in comparison with γ -Ca₃(PO₄)₂. θ_i is the solid angle subtended by the i -th face of *O'Keeffe-Voronoi polyhedron*.

	γ -Ca ₃ (PO ₄) ₂ ^a	Sr ₃ (PO ₄) ₂	Ba ₃ (PO ₄) ₂
M(1) polyhedron			
θ_i ($^\circ$) M(1)-O(1) (x6)	0.600	0.652	0.684
-O(2) (x6)	1.495	1.442	1.410
Mean bond length(\AA)	2.739	2.842	2.986
Weighted mean bond length(\AA)	2.612	2.740	2.900
M(2) polyhedron			
θ_i ($^\circ$) M(2)-O(1)	1.980	1.838	1.747
-O(2) (x3)	1.391	1.300	1.233
-O(2) (x6)	1.069	1.138	1.187
Mean bond length(\AA)	2.588	2.700	2.850
Weighted mean bond length(\AA)	2.556	2.684	2.841

a) Sugiyama and Tokonami (1988)

4 in comparison with those of high pressure phase of $\text{Ca}_3(\text{PO}_4)_2$ (Sugiyama and Tokonami, 1988). The variance of the solid angle for each bond and the difference between the weighted and unweighted mean bond lengths indicate that the distortion around two metal sites tends to decrease with increasing ionic radius in the order of Ca, Sr and Ba. It should be noted that this change accompanies the increased contribution of the M(1)-O(1) bond so as to compensate the decrease in the relative bond strength of the M(2)-O(1) bond.

The adaptability of these polyhedra to a change in ionic size may, in turn, be one of the most important characteristics of this structure. Further structural studies of this type of materials with various large lithophile elements are required for discussing the geochemical role of calcium orthophosphate in the earth's mantle.

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